

Investigation of the Performance of
Sulfation and Nitration Plates

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INVESTIGATION OF THE PERFORMANCE OF
SULFATION AND NITRATION PLATES

by

J. E. Sickles, II

and

R. M. Michie

Research Triangle Institute
Research Triangle Park, North Carolina 27709

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Project Officer

J. W. Spence

EMCD

Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are released in large quantities by anthropogenic sources. These gases are the major precursors of the acids which contribute to acidic precipitation. Inexpensive, reliable, and accurate means are needed to monitor SO_2 and NO_2 in the atmosphere.

One type of method which has been used with varying degrees of acceptance for two decades is the passive reactive monitor. Such a device is exposed for a period of time where the pollutant in the surrounding ambient air reacts with the reactive surface of the monitor. A quantitative chemical determination of the reaction product is made, and a calibration factor is then applied to estimate the pollutant concentration in the ambient air averaged over the exposure period.

Passive monitors for SO_2 and NO_2 are available from commercial suppliers. These devices are known as sulfation and nitration plates. The objects of the current study are to evaluate the performance of commercial sulfation and nitration plates. The study is designed to determine the sensitivity of plate calibration factors to pollutant concentration, simulated wind speed, humidity, and temperature.

Test results indicate that for sulfation and nitration plates, sulfation calibration factors are extremely sensitive to wind speed. A slight effect of relative humidity was observed for sulfation calibration factors on both types of plates and for nitration calibration factors on nitration plates. Nitration calibration factors are extremely sensitive not only to wind speed, but to NO_2 concentration and temperature as well.

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SECTION 1

INTRODUCTION

Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are released in large quantities by anthropogenic sources. These gases are the major precursors of the acids which contribute to acidic precipitation. Inexpensive, reliable, accurate means are needed to monitor SO_2 and NO_2 in the atmosphere.

One type of method which has been used with varying degrees of acceptance for two decades is the passive reactive monitor. Such a device is exposed for a period of time where the pollutant in the surrounding ambient air reacts with the reactive surface of the monitor. The monitor is then returned to the laboratory where a chemical determination of the reaction product is made. By considering the duration of exposure and the reactive surface area, a product flux (F) is determined. This product flux is used along with a calibration factor (CF) to estimate the gas phase concentration of the pollutant (C). Historically this calibration factor, which relates ambient air pollutant concentration to product flux ($CF = C \div F$), has been assumed to be constant. The magnitude of this calibration factor may depend on several variables, such as pollutant concentration, wind speed, humidity, and temperature.

Passive monitors for SO_2 and NO_2 are available from commercial suppliers. These devices are known as sulfation and nitration plates. The objects of the current study are to evaluate the performance of commercial sulfation and nitration plates. The study is designed to determine the sensitivity of plate calibration factors to pollutant concentration, simulated wind speed, humidity, and temperature.

SECTION 2

CONCLUSIONS

The performance of commercially available passive monitors for SO_2 and NO_2 has been evaluated. Sulfur dioxide is collected as SO_4^{2-} on both sulfation and nitration plates. Nitrogen dioxide is collected effectively only on the nitration plates and is retained as NO_2^- . Nitration plates are subject to SO_4^{2-} and NO_2^- loss upon storage and should be analyzed promptly after use. No SO_4^{2-} loss was observed for sulfation plates.

The percentage changes in calibration factors (CF) corresponding to changes in the tested environmental variables are given in Table 1 along with precision estimates. Sulfation CF, for both types of plates, are relatively independent of SO_2 concentration and temperature. They are dependent on wind speed and relative humidity. They are also subject to appreciable lot-to-lot differences and for sulfation plates to smaller within-lot, plate-to-plate differences. As the simulated wind speed was reduced from 4.7 to 0.7 m/sec, the CF increased by factors of 3.1 and 4.5 on sulfation and nitration plates. As the relative humidity was reduced from 79 to 16 percent, the sulfation CF increased on the average by 45 percent for sulfation and nitration plates. The lot-to-lot precision of SO_2 deposition to nitration plates was better than one percent; while for sulfation plates this difference averaged 30 percent. At room temperature, the within-lot, plate-to-plate variability of SO_2 deposition to sulfation and nitration plates averaged 4.5 percent at the high velocity test condition and 15 percent at the low velocity test condition.

Nitration CF are sensitive to most of the tested variables. As the NO_2 concentration was increased from 20 to 200 ppb, the CF increased by a factor of 2.5. As the simulated wind speed was reduced from 4.7 to 0.7 m/sec, the CF increased by a factor of 2.4. Reducing the relative humidity from 79 to 16 percent increased the nitration CF by 67 percent. A temperature change from 27°C to 5.6°C increased the CF by a factor of 4.6 at the higher wind speed and 2.9 at the lower wind speed.

Table 1. Summary of the Sensitivity and Precision of Calibration Factors for Sulfation and Nitration Plates

Plate Type	Calibration Factor	Percentage Change in CF Corresponding to Indicated Change of Environmental Variable				Precision (%)	
		Concentration 20 to 200 ppb	Wind speed 4.7 to 0.7 m/sec	Humidity 79 to 16% RH	Temperature 27 to 5.6°C	Lot-to-Lot	Plate-to-Plate Within-Lot
Sulfation	CF _{SO₄²⁻}	+25	+310	+39	negligible ^a	+30	b +5.3 +16 ^c
Nitration	CF _{SO₄²⁻}	+15	+450	+49	negligible ^a	negligible ^a	b +3.5 +14 ^c
Nitration	CF _{NO₃⁻}	+250	+240	+67	b +460 +290 ^c	negligible ^a	b +2.7 +7.5 ^c

^a On the average the difference is less than 5%.

^b Result is for the high velocity wind speed.

^c Result is for the low velocity wind speed.

The lot-to-lot variation in nitration CF is small and was found to be less than three percent. At room temperature the within-lot, plate-to-plate variability of NO₂ deposition to nitration plates averaged 2.7 percent at the high wind speed and 7.5 percent at the lower wind speed.

Test results indicate that for either sulfation or nitration plates, sulfation CF are extremely sensitive to wind speed. Nitration CF are extremely sensitive not only to wind speed, but to NO₂ concentration and temperature as well.

These findings identify and quantify many of the uncertainties associated with the use of sulfation or nitration plates in ambient air quality monitoring. They should provide insight toward the interpretation of data collected using such devices. Finally, these results should provide guidance as to the quality of information that can be expected from these devices if their deployment is considered in future air quality studies.

SECTION 3

RECOMMENDATIONS

The work completed to date has revealed much about the response of commercial sulfation and nitration plates to known atmospheres containing NO_2 and SO_2 . It has identified several potential problems associated with the use of such devices under a variety of simulated environmental conditions. Lot-to-lot differences for sulfation plates were observed. When plates are deployed in the field, they are exposed on a support rack that is aerodynamically different from their more idealized exposure configuration in the wind tunnel of the current study. The current approach focused heavily on the empirical determination of calibration factors and as a result is amenable to more fundamental analysis. These considerations point toward areas where additional study is warranted.

- o Conduct replicate testing in an attempt to get representative estimates of lot-to-lot and manufacturer-to-manufacturer differences in CF.
- o Investigate the interaction of the support rack and plate position on pollutant deposition using the wind tunnel.
- o Examine the fundamental behavior of the deposition process by confirming the rate-controlling step through experiments at several velocities and by modeling the results using fluid flow and mass transfer considerations.
- o Use the findings of the current study (e.g., the extreme sensitivity to wind speed) to select/design more appropriate passive samplers that would not suffer the shortcomings of the currently available devices.

SECTION 4

EXPERIMENTAL

An exposure apparatus was designed and built which permits the simultaneous exposure of up to 40 plates with half exposed at a high gas velocity and half at a low gas velocity. Plexiglas and stainless steel are the materials of construction. As indicated in Figure 1, the test atmosphere is recirculated through the test section. Additionally, there is a feed and a bleed stream where the pollutant concentration is maintained at a constant level by controlling the pollutant flow rate into the feed stream. The test section is approximately 152 cm long, it contains two parallel channels, and each channel has dimensions of 6.35 by 10.2 cm. A baffle at the end of one channel effects the velocity difference. The test apparatus was contained in a temperature-controlled environmental chamber which can maintain the temperature to within $\pm 0.5^{\circ}\text{C}$.

Air sampling occurs both up and downstream of the test section on a 30-minute cycle as controlled by a Chronotrol timer. A Monitor Labs Model 8440 Nitrogen Oxides Analyzer and Model 8450 Sulfur Monitor were used to determine the pollutant concentrations in the test apparatus. An EG&G Model 880 was used to monitor dew point, and a shielded thermistor was used to measure temperature.

A Thermo-Systems, Inc. Anemometer and a Datametric Barocel Electronic Manometer with a pitot tube were used to monitor gas velocity in the test section. In the high velocity (HV) channel the gas velocity at the centroid averaged 471 cm/sec, and in the low velocity (LV) channel the centroidal velocity averaged 66.6 cm/sec. Friction velocities were determined by two techniques to be 18 and 21 cm/sec in the HV channel and 2.4 and 4.0 cm/sec in the LV channel.

Sulfation and nitration plates were acquired from SERCO (P. O. Box 625, Cedar Falls, Iowa 50613) for testing. The sulfation plate is a 5.0 cm diameter petri dish with a lead dioxide (PbO_2) coating. The nitration plate is identical to the sulfation plate, except it has a coating of triethanolamine (TEA).

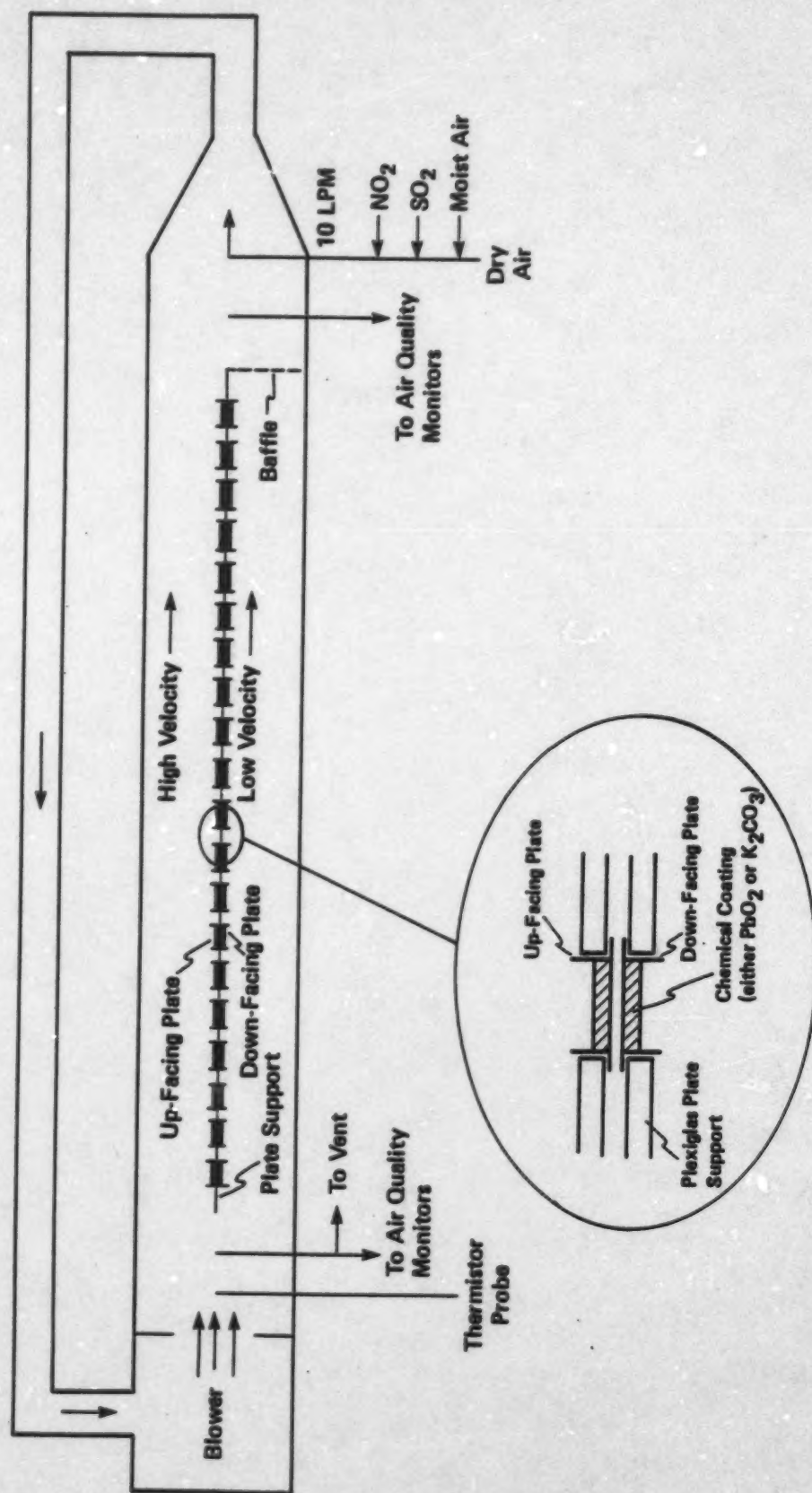


Figure 1. Schematic of exposure apparatus.

The experimental program is summarized in Table 2. Nominal pollutant concentrations of 20, 50, and 200 ppb were used. The tabulated values represent a mean of hourly averages determined over the duration of each test. Except for the first test, they exhibit good precision, generally better than 10 percent. Plates were exposed under test conditions for nominal periods of one to two weeks. Gas velocities of 4.7 and 0.7 m/sec were used. In the first five exposures, nominal test conditions of 26°C and 45 percent relative humidity were employed. Tests 6 and 7 were conducted at the same temperature, but at different relative humidities -- 79 and 16 percent. Test 8 was conducted at a lower temperature, 5.6°C, and at 48 percent relative humidity.

Each plate was desorbed in 50 mL of sodium bicarbonate-sodium carbonate eluent solution. The solutions were subjected to nitrite (NO_2^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) analysis by ion chromatography (IC).

IC analysis provides a direct measure of pollutant reaction product loading in units of $\mu\text{g}/\text{plate}$. By using the area per plate (20.27 cm^2) and the duration of exposure (day), the product flux in units of $\mu\text{g}/\text{cm}^2 \text{ day}$ is determined. The pollutant gas phase concentration is determined by the gas monitor and converted from ppb into $\mu\text{g}/\text{m}^3$. The calibration factor is simply the ratio of the gas concentration to the product flux. It should be noted that the reciprocal of the calibration factor (adjusted by the appropriate stoichiometry and molecular weight) may be expressed as the deposition velocity in cm/sec .

Table 2. Summary of the Experimental Program

Test Number	Type	Mean Concentration			Test Duration		Velocity, cm/sec		Temperature °C	Relative Humidity %
		ppb	µg/M ³	CV, %	hr	Day	HV	LV		
1	S ^a	53.9 ^c	141	91.0	250	10.4	457	68.4	25.8	48.1
	N ^b	0.0 ^c	0	d	250	10.4	457	68.4	25.8	48.1
2	S	0.0	0	d	166	6.92	466	69.3	26.4	42.1
	N	47.0	88.4	9.2	164	6.83	466	69.3	26.4	42.1
3	S	49.0	128	10.4	162	6.75	476	65.0	27.2	40.6
	N	51.0	95.9	6.7	162	6.75	476	65.0	27.2	40.6
4	S	207	541	5.1	144	6.00	473	66.7	26.0	45.5
	N	194	365	3.1	144	6.00	473	66.7	26.0	45.5
5	S	22.3	58.3	5.4	357	14.9	469	64.3	26.3	42.0
	N	21.6	40.6	10.6	357	14.9	469	64.3	26.3	42.0
6	S	50.5	131	3.2	144	6.00	490	67.8	26.0	78.7
	N	51.3	95.8	5.8	144	6.00	490	67.8	26.0	78.7
7	S	51.8	135	4.0	144	6.00	479	67.0	26.0	15.5
	N	50.6	94.5	10.5	144	6.00	479	67.0	26.0	15.5
8	S	50.1	140	2.2	144	6.00	460	64.4	5.6	48.2
	N	50.6	102	6.2	144	6.00	460	64.4	5.6	48.2

^aS = Sulfation.

^bN = Nitration.

^cThe species concentrations corresponding to S and N are for SO₂ and NO₂; the tabulated value is the mean of hourly average concentrations determined over the duration of the test.

SECTION 5

QUALITY ASSURANCE

ANALYZERS

The NO_x and SO_x analyzers were subjected to four-point calibrations before and after each test. At least one zero and span check was performed during each test.

ION CHROMATOGRAPHY

Calibration of the IC was performed daily. Independently prepared quality control samples were submitted along with regular samples for IC analysis. Difference analysis of the resulting data showed the analyses to be unbiased with precision of 5 percent or better. Time series analysis showed no apparent trends.

DESORPTION METHODOLOGY

Duplicate blank plates and duplicate spiked plates were desorbed and analyzed. The precision as indicated by an average coefficient of variation for 16 paired measurements is 2.6 percent. Analysis of spiked plates showed between 90 and 110 percent recovery of the added species. This adds confidence to the desorption and analytical methodology.

UNEXPOSED BLANKS

Blank sulfation and nitration plates were analyzed. The background NO_2^- , NO_3^- , SO_4^{2-} levels on the tested plates differed from experiment to experiment. These levels on sulfation plates ranged from 19, 172, 264 $\mu\text{g}/\text{plate}$ in the first four experiments to 19, 47, and 49 $\mu\text{g}/\text{plate}$ in the last four experiments. The corresponding levels for the tested nitration plates are 19, 170, 283 $\mu\text{g}/\text{plate}$ in the first four experiments and 13, 11, and 22 $\mu\text{g}/\text{plate}$ in the last four experiments. No lot-to-lot differences in background levels are apparent for either type of plate.

EXPOSED BLANKS

Comparison of unexposed blank plate results with data from plates exposed during the first four experiments reveals several points of interest. Exposure of sulfation plates to NO_2 gives NO_2^- , NO_3^- , SO_4^{2-} loadings which do not differ appreciably from the background levels of the unexposed plates. This suggests that sulfation plates are essentially inert to NO_2 . The addition of SO_2 to the above NO_2 -laden gas has no effect on the NO_2^- and NO_3^- loadings of sulfation plates.

Analysis of nitration plates exposed to NO_2 and NO_2 - SO_2 mixtures indicates that NO_3^- loadings do not differ from the unexposed plates, and deposited NO_2 is recovered as NO_2^- , not NO_3^- . The NO_3^- loadings from the last four experiments are lower than the results from the first four experiments. This difference remains to be reconciled.

Exposed plates do not show a humidity or temperature dependence for NO_2^- and NO_3^- loadings on sulfation plates or NO_3^- loadings on nitration plates. In addition, experiments where SO_2 was exposed to both nitration and sulfation plates show comparable SO_2 deposition on both types of plates.

STABILITY AFTER STORAGE

Fifty selected plates exposed during the first three tests were covered, set aside, and stored at room temperature for approximately nine months. Twenty plates were sent to SERCO for analysis. Thirty plates were retained by RTI. They were then desorbed and analyzed in the usual manner. Results of the initial and final RTI analyses were compared to determine the stability of exposed plates after storage. On the average, an 11 percent deficit of SO_4^{2-} and a 32 percent deficit of NO_2^- was found on nitration plates after 9.5 months of storage. No appreciable difference in SO_4^{2-} was found on sulfation plates over the same period. Thus, nitration plates are more subject to storage problems than are sulfation plates.

COMPARISON OF SO_4^{2-} AND NO_2^- DETERMINATIONS BY RTI AND SERCO

Of the 20 plates shipped to SERCO for analysis, 8 were sulfation plates and 12 were nitration plates. Results of RTI analyses of the 30 plates were compared to those of SERCO for the 20 plates. Comparisons were drawn using a ratio of results -- SERCO/RTI. The average SERCO/RTI ratio for NO_2 deposition to nitration plates was 1.43 (+16%). The average SERCO/RTI ratio for SO_2 deposition to nitration plates was 1.60 (+44%) and to sulfation plates was 1.55 (+13%). Thus, the SERCO results were 50 percent higher than the RTI results on the average.

SECTION 6

RESULTS

DEPOSITION GRADIENT IN TEST SECTION

Results from plate analysis are shown for the first test in Figure 2. The SO_4^{2-} concentration in the 50 mL of desorption solution from each plate is given as a function of the plate's longitudinal position in the exposure apparatus. These results show: more SO_4^{2-} is deposited at HV than at LV; there is substantial lot-to-lot difference in SO_4^{2-} deposition on sulfation plates; SO_2 deposition is comparable on sulfation and nitration plates; and a decreasing trend in deposition exists with position down the exposure apparatus which becomes negligible beyond position number seven. This "position effect" is more pronounced at LV than HV and may reflect the sensitivity of deposition at LV to turbulence at the entrance to the test section. As a result of this finding, subsequent tests were conducted with dummy plates in the first seven positions, and only the last 13 positions were used to expose authentic plates.

PRODUCT FLUX

Based on the plate analyses, product fluxes were determined and are given in Table 3. Since each of these entries is based on multiple plate exposures and analyses, the coefficient of variation and number of plate analyses upon which it is based were determined. These results are presented in Table 4. For the tests conducted at room temperature, on the average, the precision for determining NO_2 deposition is 3 to 8 percent while the precision for SO_2 deposition is 4 to 16 percent. These estimates are consistent with the CV of 12 percent reported for 47 paired sulfation plates exposed in the field¹. The tabulated results also suggest that precision is dependent on velocity with the HV results having higher precision than the LV

¹ Vandenberg, J. J. and K. R. Knoerr (1982). Dry Deposition of Sulfate to Surrogate and Natural Surfaces Within and Above a Hardwood Forest Canopy. Duke University. Final Report on EPA Grant No. R-806393.

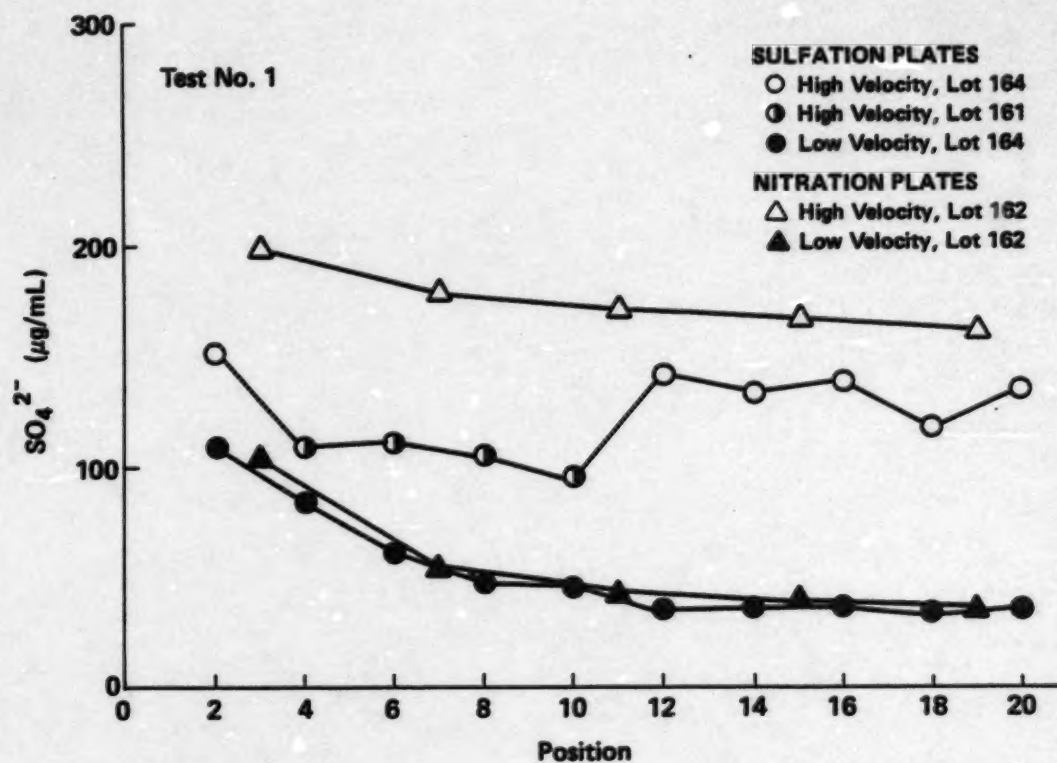


Figure 2. Sulfate concentration in the desorption solution of each plate in Test No. 1 as a function of plate position.

Table 3. Summary of Flux Data^a

Test	Nitration Plates					Sulfation Plates		
	Lot	NO ₂ ⁻		SO ₄ ²⁻		Lot	SO ₄ ²⁻	
		HV	LV	HV	LV		HV	LV
1	162	----	----	38.81	8.97	164	31.59	9.19
	---	----	----	-----	----	161	25.02	----
2	162	1.91	0.72	-----	----	160	-----	----
3	162	2.25	0.93	33.21	6.19	160	24.51	7.06
4	162	5.10	2.36	126.27	28.68	164	83.31	29.13
	163	4.96	2.30	125.96	28.23	161	60.84	23.36
5	162	1.49	0.58	14.64	3.61	164	12.10	3.61
	163	1.49	0.60	14.80	3.62	161	8.55	2.94
6	162	2.79	1.30	36.39	9.04	164	32.66	7.22
7	162	1.60	0.79	29.86	5.38	164	19.27	7.19
8	162	0.52	0.34	33.82	6.56	164	27.72	7.73

^a Units = $\mu\text{g}/\text{cm}^2$ day

Table 4. Precision Summary of Plate Determinations of Product Deposition^a

Test	Nitration Plates					Sulfation Plates		
	Lot	NO ₂ ⁻		SO ₄ ²⁻		Lot	SO ₄ ²⁻	
		HV	LV	HV	LV		HV	LV
1	162	----	----	4.6 (4)	9.4 (3)	164	6.8 (5)	14.9 (7)
	---	----	----	----	----	161	7.1 (4)	----
2	162	3.9 (4)	10.3 (4)	----	----	160	----	----
3	162	3.7 (4)	4.3 (3)	3.5 (4)	10.6 (3)	160	8.8 (5)	20.7 (4)
4	162	2.9 (4)	6.0 (4)	3.2 (4)	18.2 (4)	164	5.5 (4)	22.3 (4)
	163	1.1 (2)	7.2 (2)	0.6 (2)	10.6 (2)	161	3.1 (2)	15.3 (2)
5	162	1.6 (5)	8.0 (5)	4.5 (5)	23.2 (5)	164	4.4 (4)	18.9 (4)
	163	1.5 (2)	3.9 (2)	5.0 (2)	4.2 (2)	161	2.4 (2)	7.3 (2)
6	162	3.4 (6)	7.0 (6)	2.3 (6)	14.2 (6)	164	5.8 (6)	11.5 (6)
7	162	3.6 (6)	13.0 (6)	4.6 (6)	23.0 (6)	164	4.2 (6)	18.0 (6)
8	162	33.9 (5)	42.2 (5)	12.3 (5)	28.1 (5)	164	10.8 (5)	17.9 (5)
Average ^b ---								
		2.7 (8)	7.5 (8)	3.5 (8)	14.2 (8)	---	5.3 (9)	16.1 (8)

^a Tabulated entries are coefficients of variation in percent, and the entries in parenthesis represent the number of plate determinations considered.

^b Tabulated averages are for the tests performed at room temperatures; results from Test 8 are not included.

results, that nitration plates are slightly more precise than sulfation plates for quantifying SO_2 deposition, and that NO_2 deposition on nitration plates is more precise than SO_2 deposition on either sulfation or nitration plates.

The results in Table 4 also show that the precision of the NO_2 deposition determination is dependent on temperature. Much more variability is apparent at the lower temperature than at the higher temperature of the first seven experiments. In contrast, the precision of SO_2 deposition determination appears to be less sensitive to temperature. Examination of individual data revealed that the variability in the deposition determinations for Test 8 appears to be associated more with a trend than with random measurement error. The deposition is decreasing with distance down the chamber more strongly than in any of the earlier experiments. This may be reflecting a change in the rate-controlling step with temperature reduction.

CALIBRATION FACTORS

The gas phase pollutant concentration data from Table 2 and the product flux data from Table 3 are combined to give a CF for each test. The results are given in Table 5 and Figures 3 and 4.

Sulfation CF shown in Figure 3 are independent of SO_2 concentration but are dependent on gas velocity across the plate and on lot-to-lot differences. As the SO_2 concentration varies by a factor of ten at a given velocity, the within-lot variation in the sulfation CF is relatively small. For the sulfation plates this variation is less than 25 percent as indicated by a coefficient of variation. For the nitration plates the variation is less than 15 percent; and there is negligible difference across lots.

Differences in gas velocity exert a major influence on sulfation CF. The decrease in gas velocity by 86 percent from 4.7 to 0.7 m/sec results in an average increase of 4.45 (+11%) and 3.11 (+12%) in sulfation CF for nitration and sulfation plates.

Table 5. Summary of Calibration Factors

Test	Nitration Plates						Sulfation Plates					
	Lot	CF NO ₂ ^a		Ratio	CF SO ₄ ^{2-b}		Ratio	Lot	CF SO ₄ ²⁻		Ratio	
		HV	LV		HV	LV			HV	LV		
1	162	----	----	----	3.58	15.5	4.33	164	4.46	15.3	3.44	
2	162	46.3	122.8	2.68	----	----	----	161	5.64	----	----	
3	162	42.6	103.1	2.41	3.85	20.7	5.36	160	5.22	18.1	3.47	
4	162	71.6	154.7	2.16	4.28	18.9	4.40	164	6.49	18.6	2.86	
5	163	73.6	158.7	2.16	4.30	19.2	4.46	161	8.89	23.2	2.60	
6	162	27.2	70.0	2.57	3.98	16.2	4.06	164	4.82	16.2	3.35	
7	163	27.2	67.7	2.49	3.94	16.1	4.09	161	6.82	19.8	2.91	
8	162	34.3	73.7	2.15	3.60	14.5	4.03	164	4.01	18.1	4.51	
	162	59.1	119.6	2.02	4.52	25.1	5.55	164	7.01	18.8	2.68	
	162	196.2	300.0	1.53	4.14	21.3	5.15	164	5.05	18.1	3.58	

$^a\text{CF}_{\text{NO}_2^-} = \text{Conc } [\mu\text{g NO}_2/\text{m}^3]/\text{Flux } [\mu\text{g NO}_2^-/\text{cm}^2 \text{ day}]$

$^b\text{CF}_{\text{SO}_4^{2-}} = \text{Conc } [\mu\text{g SO}_2/\text{m}^3]/\text{Flux } [\mu\text{g SO}_4^{2-}/\text{cm}^2 \text{ day}]$

CRatio = CF at LV/CF at HV

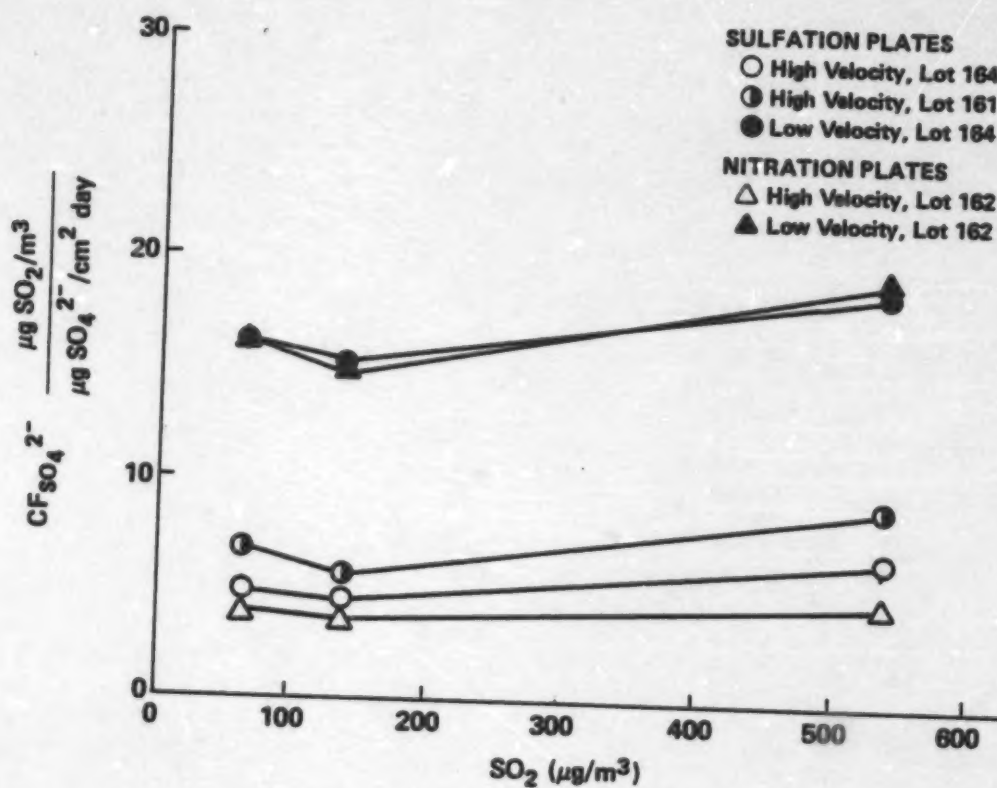


Figure 3. Sulfation CF at two velocities for sulfation plates (Lot 164) and nitration plates (Lot 162) as a function of SO_2 concentration.

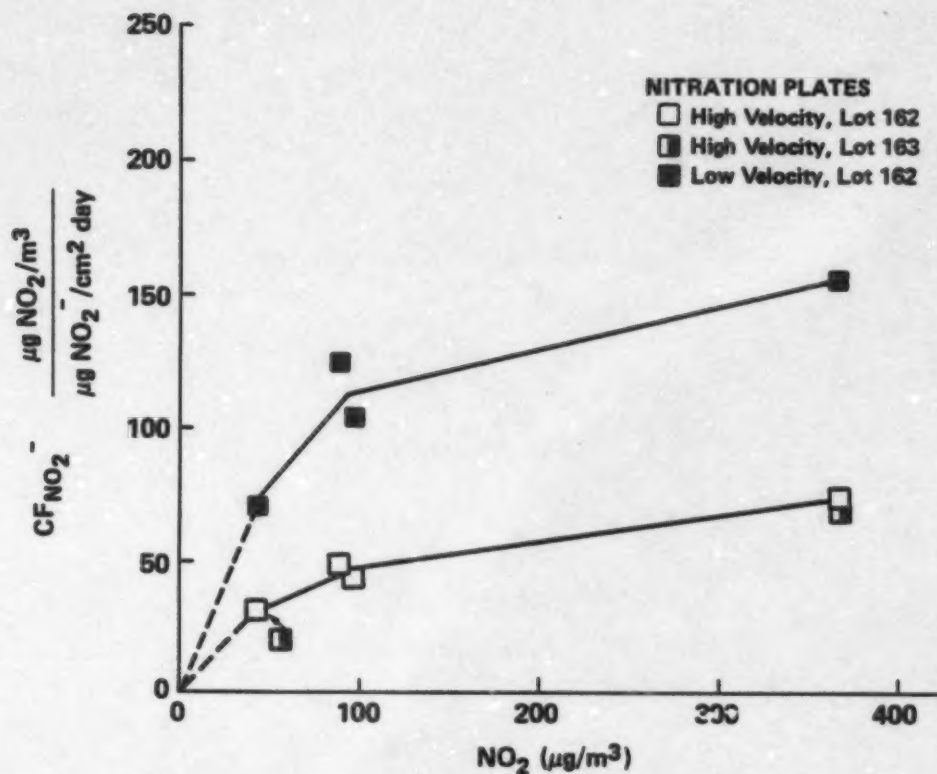


Figure 4. Nitration CF at two velocities for nitration plates (Lot 162) as a function of NO₂ concentration.

Lot-to-lot variation is appreciable for sulfation plates but not for nitration plates. Sulfation plates from three lots were tested, although comparisons could be drawn for only two lots. On the average, across five comparisons and three tests, the CF for sulfation plates from Lot 161 exceeds that from 164 by 30 percent. Nitration plates from two lots (162 and 163) were tested. On the average across four comparisons and two tests, the difference in sulfation CF is less than one percent.

Nitration CF shown in Figure 4 are dependent on both NO_2 concentration and on gas velocity across the plate but are relatively independent of lot-to-lot differences. As the NO_2 concentration increases by an order of magnitude from 20 to 200 ppb, the CF increases by a factor of 2.3 at LV and by a factor of 2.7 at HV. It is unclear if the concentration dependence as seen in Figure 4 should be extrapolated to the origin.

The decrease in gas velocity from 4.7 to 0.7 m/sec results in an average increase of 2.41 in the CF. This increase is relatively insensitive to NO_2 concentration and is constant to within nine percent over an order of magnitude change in NO_2 concentration.

Nitration plates from two lots were tested. As indicated in Figure 4, the lot-to-lot variation is small. On the average, across four comparisons and two tests, the difference in nitration CF was less than three percent.

DEPOSITION VELOCITIES

Calibration factors from Table 5 were converted to deposition velocities and are presented in Table 6. Deposition velocity is simply proportional to the reciprocal of the CF where the proportionality constant accounts for reaction stoichiometry and the conversion of days to seconds. As indicated in the table, the deposition velocity for SO_2 ranges from 0.3 to 2.2 cm/sec. It is comparable for both sulfation and nitration plates, it increases with velocity, but at fixed simulated wind speeds it is independent of SO_2 concentration.

Table 6. Summary of Deposition Velocities (cm/sec)

Test	Nitration Plates					Sulfation Plates		
	Lot	$v_{dNO_2}^a$		$v_{dSO_2}^b$		Lot	v_{dSO_2}	
		HV	LV	HV	LV		HV	LV
1	162	----	----	2.16	0.50	164	1.73	0.50
	---	----	----	----	----	161	1.37	----
2	162	0.25	0.094	----	----	160	----	----
3	162	0.27	0.112	2.00	0.37	160	1.48	0.43
4	162	0.16	0.075	1.80	0.41	164	1.19	0.42
	163	0.16	0.073	1.79	0.40	161	0.87	0.33
5	162	0.43	0.165	1.94	0.48	164	1.60	0.48
	163	0.43	0.171	1.96	0.48	161	1.13	0.39
6	162	0.34	0.160	2.14	0.53	164	1.92	0.43
7	162	0.20	0.100	1.71	0.31	164	1.10	0.41
8	162	0.059	0.039	1.86	0.36	164	1.53	0.43

$$^a v_{dNO_2} = [CF_{NO_2} \times 8.64 \times 10^{-2}]^{-1}$$

$$^b v_{dSO_2} = [CF_{SO_2} \times 0.1296]^{-1}$$

The deposition velocity for NO_2 is much less than that for SO_2 and ranges from 0.04 to 0.45 cm/sec. Not only is it strongly dependent on gas velocity, as was the deposition velocity for SO_2 , but it is also dependent on NO_2 concentration and temperature. The deposition velocity increases with decreasing NO_2 concentration or with increasing temperature.

CHAMBER-AVERAGED DEPOSITION VELOCITIES

Deposition velocities given in Table 6 were used to arrive at chamber-averaged values. These deposition velocities, based on plate analyses, v_{dp} , are given in Table 7.

Chamber-averaged deposition velocities were also estimated by a second technique. These estimates, based on pollutant mass balance, v_{dMB} , are also given in Table 7. Pollutant deposition rates were determined for the exposure apparatus in the presence and absence of plates, based on mass balance considerations and measured gas phase pollutant concentrations. The pollutant deposition rate to the plates was then determined by difference. The overall flux was determined from the deposition rate to the exposed reactive plates and their total surface area. The overall flux was divided by the pollutant gas concentration to give an estimate of the chamber-averaged deposition velocity, v_{dMB} . These estimates, as given in Table 7, are independent of the IC determination of pollutant deposition to the plates and the resulting v_{dp} .

The mass balance approach involves using the difference between two measured values. In general, this approach potentially has more opportunity for error than the more direct approach using plate analysis. The agreement is nevertheless good for the chamber-averaged deposition velocities based on plate analysis and on mass balance. Except for the low temperature test, v_{dMB} exceeds the v_{dp} , on the average, by 28 ± 10 percent. This internal consistency adds confidence to the quality of the overall data set and the techniques employed.

Table 7. Comparison of Chamber-Averaged Deposition Velocities

Test Number	Type	v _{dp}		Deposition Rate, $\mu\text{g}/\text{min}$		Plate Area cm^2	Flux $\times 10^5$		Concentration		v _{dB}		Ratio $v_{\text{dB}}/v_{\text{dp}}$
		cm/sec		With Plates	Without Plates		$\mu\text{g}/\text{cm}^2\text{-sec}$		$\mu\text{g}/\text{m}^3$		cm/sec		
1	S ^a	1.19		NAC	NA	810	NA		141 ^d		NA		NA
2	N ^b	----		----	----	----	----		0 ^d		----		----
3	S	0.17		0.64	0.10 ^e	405	2.22		88.4		0.25 ^f		1.47
3	S	1.07		10.74	1.71	810	18.6		128		1.45		1.36
4	N	0.19		0.66	0.10	405	2.31		95.9		0.24		1.26
4	S	0.92		22.63	2.87	527	62.5		541		1.15		1.25
5	N	0.12		1.10	0.28	263	5.20		365		0.14		1.17
5	S	0.97		2.62	0.34	527	7.21		56.3		1.24		1.28
6	N	0.27		0.268	0.054	263	1.36		40.6		0.33		1.22
6	S	1.26		8.57	2.59	486	20.5		131		1.57		1.25
7	N	0.25		0.831	0.444	243	2.65		95.8		0.28		1.12
7	S	0.88		4.99	0.32	486	16.0		135		1.19		1.35
8	N	0.15		0.288	0.0	243	1.98		94.5		0.21		1.40
8	S	1.14		7.98	1.42	486	22.5		140		1.61		1.41
8	N	0.064		0.252	0.0	284	1.48		102		0.14		2.19

^aS = Sulfation.

^bN = Nitration.

^cNA = Not Available.

^dThe species concentration corresponding to S and N are for SO₂ and NO₂; the tabulated value is taken from Table 2.

^eEstimated based on the results of Test 3.

^fEstimated; see Footnote e.

RELATIVE HUMIDITY

The influence of different relative humidities on calibration factors is shown in Figure 5 for high velocity tests and in Figure 6 for low velocity tests. These results indicate that with only one exception, nitration and sulfation CF increase appreciably with decreased humidity. Since only a single comparison is available, attempts at discriminating the interactions of humidity, velocity, and plate type on CF are not warranted. Thus, the impact of humidity is examined only in an average sense. As the relative humidity decreases from 79 to 16 percent, the calibration factors increase by an average of 52 ± 30 percent.

This humidity effect can be viewed with more physical significance by considering its influence on deposition velocity rather than CF. Thus, increasing the humidity by 5-fold increases the deposition velocities of SO_2 and NO_2 to the tested surfaces by approximately 50 percent. This simply suggests that increased amounts of moisture on the collection surfaces at higher humidities act to retain SO_2 and NO_2 molecules that strike the surface more effectively than would occur on drier surfaces.

TEMPERATURE

The influence of temperature on calibration factors may be inferred by inspecting Tables 5 and 6 and comparing the results of Test 3 (27°C and 41% RH) with Test 8 (5.6°C and 48% RH). Reducing the exposure temperature by 22°C from 27 to 5.6°C has no appreciable effect on the deposition of SO_2 to either nitration or sulfation plates. In contrast, deposition of NO_2 is significantly influenced by temperature reduction. The nitration CF is significantly increased by the temperature reduction -- by a factor of 4.6 at the HV and a factor 2.9 at the LV. This temperature reduction, likewise, results in a 78 percent reduction in the deposition velocity at HV and a 66 percent reduction at LV. The temperature sensitivity of the nitration plates may be reflecting the liquid to solid phase change that occurs for TEA around 21°C.

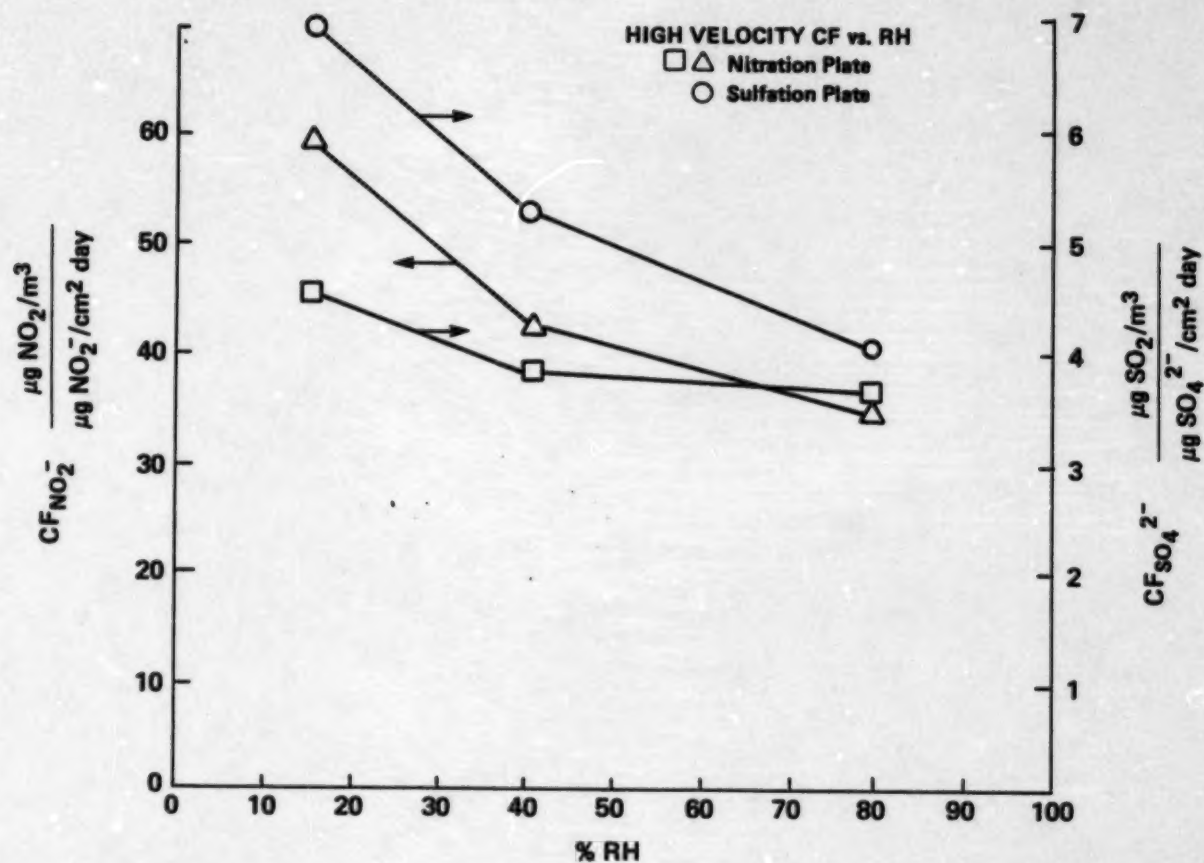


Figure 5. Sulfation and nitration calibration factors at nominal 50 ppb SO₂ and NO₂ as a function of relative humidity at high velocity conditions over sulfation and nitration plates.

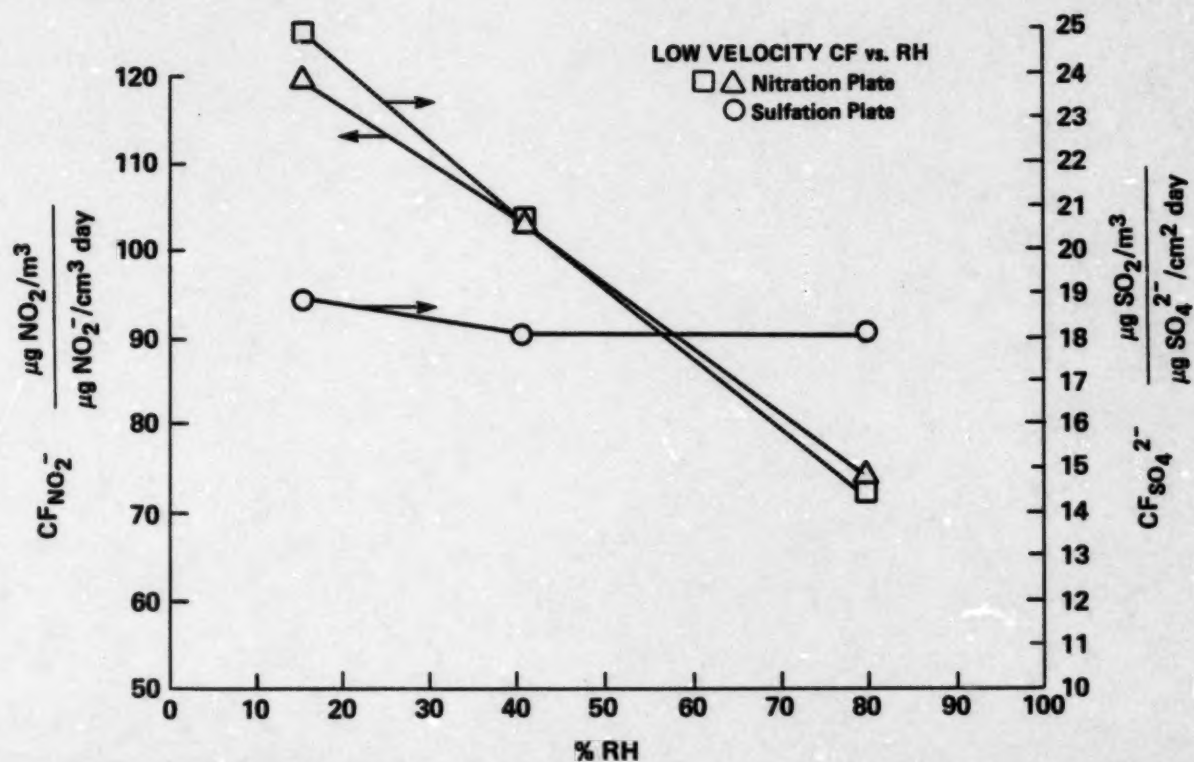


Figure 6. Sulfation and nitration calibration factors at nominal 50 ppb SO_2 and NO_2 as a function of relative humidity at low velocity conditions over sulfation and nitration plates.